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Short Communication

Polyethylene glycol-supported recyclable NC palladacycle catalyst for Heck cross-coupling reactions

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ABSTRACT

Palladium nanoparticles with narrow size distribution were easily prepared by applying polyethylene glycol (PEG 1000 and 15000) and NC palladacycle in the absence of other chemical agents. The Pd-PEG catalysts were fully characterized by a variety of techniques including X-ray diffraction (XRD), transmission electron microscopy (TEM), UV–vis and Fourier transform infrared (FT-IR) spectroscopy. TEM micrographs of Pd/PEG 15000 show that palladium nanoparticles have mostly very well-defined geometrical shapes. Also Pd/PEG 15000 was relatively an efficient catalyst system for the Heck reaction, affording a diverse range of products in moderate to good yields.

1. Introduction

The palladium-catalyzed Heck reaction developed in the early 1970s was a milestone in modern organic chemistry [1,2]. Heck reaction is normally carried out in the presence of phosphine ligands and base under an inert atmosphere. However, the relatively high price of the palladium complex has greatly limited the industrial application of homogeneous Heck reaction, and some of the phosphine ligands are sensitive to air and moisture [3,4]. Most of the problems related to homogeneous catalysts can be solved by immobilizing the catalyst or catalyst precursor on polymer supports with good solvation attributes [5].

Palladium (Pd) nanoparticles are a unique class of heterogeneous catalysts that is widely used and effective for a variety of organic reactions due to its high surface-to-volume ratio. These catalysts can be based on either supported palladium nanoparticles or supported palladium complexes on various supports, such as, carbon [6], silica [7], resin [8], chitosan [9], alumina [10], zeolite [11], and organic polymer supports [12,13].

On the other hand, palladacycles have been known as well-defined catalysts or precatalysts in cross-coupling reactions [14–16]. They can be easily prepared, show high stability under atmospheric conditions and can be anchored to different solid supports. Supported palladacycles are increasingly investigated by several research groups and being used in various organic transformations. Najera and Alacid [17,18] performed Heck and Suzuki cross-couplings using polystyrene supported oxime palladacycle in water as solvent. Luo et al. [19], used polystyrene-supported soluble palladacycle as an excellent and recyclable catalyst for Heck, Suzuki and Sonogashira reactions. The activity and stability of the PEG-anchored oxime palladacycle in coupling reactions have been also reported by Corma et al. [20].

Among polymer supported nanoparticles, polyethylene glycol (PEG) is a promising candidate which is inexpensive, nontoxic and its properties can be tuned by simply changing molecular weight [21]. Herein, in continuation of our studies in developing new supported catalysts [22,23], we report a simple and environmentally friendly route for the preparation of PEG supported NC palladacycle (Scheme 1). To the best of our knowledge, the present work is the first example of the heterogeneous nanocatalyst based on amine NC palladacycle supported on PEG. We also investigated the application of the prepared catalyst in the Heck cross-coupling reaction which was carried out in the absence of phosphine ligands under air.

2. Experimental

2.1. Instruments and reagents

All chemicals and solvents were purchased from Merck and Aldrich and used without further purification or drying. Conversions were monitored using an Agilent 6890N gas chromatograph equipped with a capillary HP-5$^+$ column, based on aryl halides. Electronic absorption spectra were recorded on a JASCO 7580 UV–vis–NIR spectrophotometer. Infrared spectra were recorded on a FT-IR JASCO 680 spectrophotometer in the spectral range 4000–400 cm^{-1} using the KBr pellets technique. X-ray powder diffraction data were collected on an XD-3A diffractometer using Cu Kα radiation. Transmission electron microscopy analyses were performed by PHILIPS (model CM120) electron microscope.

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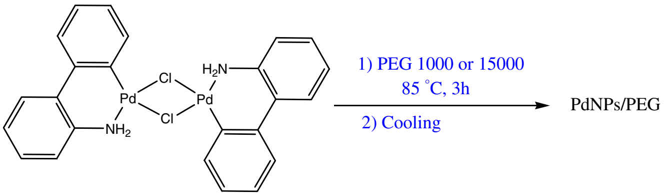


Scheme 1. Preparation of supported palladium nanoparticles (PdNPs) using different PEGs.

Palladium content of the catalyst was measured by Inductively Coupled Plasma (ICP-OES) analyzer (PerkinElmer 7300DV spectrometer). Dimeric NC palladacycle was obtained using procedure described earlier [24].

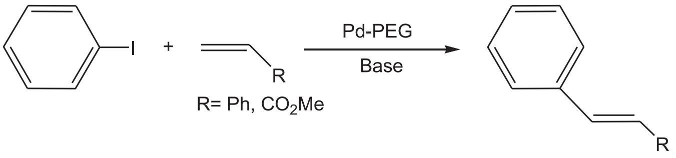
2.2. Preparation of Pd-PEG catalyst

Dimeric NC palladacycle (0.22 mmol, 0.136 g) was added into PEG (2 mmol) with different molecular weights (1000 or 15000) in a 25-mL round-bottomed flask. The mixture was heated in a water bath at 85 °C under vigorous, continuous stirring for 3 h. During this stage, the red-brown color of the solution turned to dark gray, indicating the formation of Pd nanoparticles. The mixture of Pd nanoparticles in PEG solidified upon cooling at room temperature.

2.3. General procedure for Heck reaction

A mixture of aryl halide (1.0 mmol), olefin (1.5 mmol), Et_3N (1.5 mmol), toluene (9 mL), ethanol (1 mL) and catalyst (4.5 mmol% related to aryl halides) was stirred at 80–120 °C for the time given in Tables 1 and 2. After the reaction, toluene and ethanol were removed in a rotavapor and the residue was extracted with cold ether (5 × 15 mL). The combined ether solution was taken for GC analyses.

Table 1
Heck coupling of iodobenzene with styrene and methyl acrylate: Reaction conditions study.



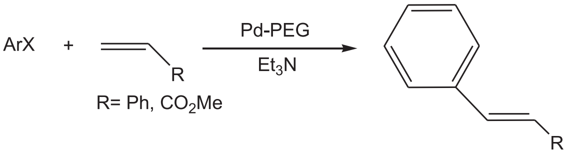
Entry	Olefin	Base	Temp (°C)/time (h)	Yield[a] (%)
1	Methyl acrylate	Na_2CO_3	80/8	Trace
2	Methyl acrylate	NaOAc	80/8	Trace
3	Methyl acrylate	KOH	80/8	Trace
4	Methyl acrylate	$K_3PO_4 \cdot 3H_2O$	80/8	Trace
5	Methyl acrylate	Et_3N	80/8	7
6	Methyl acrylate	Na_2CO_3	100/8	Trace
7	Methyl acrylate	NaOAc	100/8	Trace
8	Methyl acrylate	KOH	100/8	Trace
9	Methyl acrylate	$K_3PO_4 \cdot 3H_2O$	100/8	Trace
10	Methyl acrylate	Et_3N	100/8	17
11	Methyl acrylate	Et_3N	120/8	21
12	Methyl acrylate	Et_3N	100/16	40
13	Styrene	Na_2CO_3	100/8	4
14	Styrene	Et_3N	80/8	12
15	Styrene	Et_3N	100/8	43
16	Styrene	Et_3N	100/16	80
17	Styrene	Me_3N	100/16	9
18[b]	Styrene	Et_3N	100/16	50
19	Methyl acrylate	Et_3N	100/24	48

Reaction conditions: iodobenzene 1 mmol, olefin 1.5 mmol, base 1.5 mmol, Toluene 9 mL, ethanol 1 mL, catalyst (4.5 mmol% relative to the amount of iodobenzene).

[a] Isolated yields determined by GC, based on iodobenzene.

[b] Using Pd/PEG 1000.

Table 2
Heck coupling of aryl halides with styrene and methyl acrylate catalyzed by Pd/PEG 15000.



Entry	Ar	X	R	Yield[a] (%)
1	C_6H_5	I	C_6H_5	80
2	m-$CH_3C_6H_4$	I	C_6H_5	40
3	p-$CH_3C_6H_4$	I	C_6H_5	53
4	p-$CH_3OC_6H_4$	I	C_6H_5	68
5	C_6H_5	Br	C_6H_5	61
6	C_6H_5	Br	CO_2Me	27
7	C_6H_5	I	CO_2Me	40
8	m-$CH_3C_6H_4$	I	CO_2Me	19
9	p-$CH_3C_6H_4$	I	CO_2Me	27
10	p-$CH_3OC_6H_4$	I	CO_2Me	67

Reaction conditions: aryl halide 1 mmol, olefin 1.5 mmol, Et_3N 1.5 mmol, toluene 9 mL, ethanol 1 mL, catalyst (4.5 mmol% relative to the amount of aryl halides) at 100 °C, 16 h.

[a] Isolated yields determined by GC, based on aryl halide.

3. Results and discussion

3.1. Catalysts characterization

The crystalline structure of supported Pd-catalyst was obtained using powder XRD. The typical patterns of catalysts prepared using NC palladacycle in PEG (1000 and 15000) are presented in Fig. S1 (Supporting information). As shown in the XRD patterns, two peaks at about 19.2° and 23.4° indicated the presence of pure PEG polymer [12]. Also, broad weak peak near $2\theta = 40°$ is detected, which can be indexed to the characteristic reflection (111) plane for face-centered-cubic Pd(0) with another weak peak around $2\theta = 43°$, consistent with the (200) crystalline plane (JCPDS card no. 87-641). The broadening of the diffraction peaks as compared to that of bulk Pd indicates the formation of the palladium nanoparticles. The intensity of palladium peaks slightly increases in the case of using PEG 15000, which related to the different degrees of chemical reduction of NC palladacycle in PEGs. The crystallite size was calculated using Scherer's equation, and the values corresponding to the refection planes (111) were found to be 14.8 nm and 13.2 nm for Pd/PEG 1000 and 15000, respectively. The same result was also obtained for the XRD pattern of the Pd/PEG 15000 after its use in the Heck reaction for several cycles. This reveals the excellent stability and recovery of the catalyst.

Fig. S2 (Supporting information) displayed the UV–vis spectra of dimeric NC palladacycle before and after the reduction with different molecular weight PEGs as a reducing agent. As can be seen, the UV–vis spectrum of dimer shows absorption maximum at around 330 nm. After the reaction of Pd(II) ions with different molecular weight PEGs, the peak observed at 330 nm has strongly decreased, indicating the conversion of Pd(II) to Pd(0) nanoparticles. Also, the intensity of this peak further decreased when PEG with larger chain length was applied.

Fig. 1 presents the TEM images of palladium nanoparticles prepared at 85 °C using PEG 15000. The average dimension of Pd nanoparticles is around 2–12 nm, in good agreement with the crystallite size calculated from XRD data. As shown in Fig. 2(a), palladium nanoparticles derived from PEG 15000 have interestingly very well-defined geometrical shapes including triangle, rhombohedral, pentagonal and unidentified. Comparing to the previously reported catalysts (from various starting materials of palladium) [13,20], this typical catalyst exhibits such a distinguished shapes.

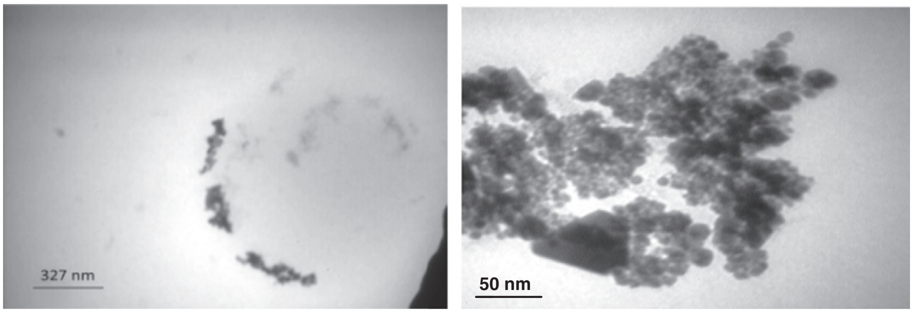


Fig. 1. TEM images of PEG 15000 stabilized palladium nanoparticles.

The formation of palladium nanoparticles by heating the NC palladacycle in PEG in the absence of any other reducing agent may proceed through the oxidation of the hydroxyl group in PEG. The analysis of PEG after the reaction by FT-IR revealed that a new absorption peak appeared at around 1739 cm^{-1}, which could be attributed to the formation of the aldehyde during the reduction of Pd(II). This is actually in agreement with a similar analysis done by ^1H NMR and confirmed the formation of aldehyde group for a similar reaction system [13].

3.2. Catalytic activity

The catalytic reactivity of Pd-PEG to Heck reaction involving the cross-coupling of aryl halides with styrene and methyl acrylate was tested. The reactions were performed in Pd-PEG by using 4.5 mmol% of the palladium related to aryl halide. Initially, the Heck reactions of iodobenzene with methyl acrylate and styrene were chosen as model reactions. Various parameters including bases, temperature and time were screened to optimize the reaction conditions (Table 1). As shown in Table 1, when the organic base Et_3N was used, good yield was obtained but longer reaction time was required (Table 1, entry 16). However, other bases gave trace yields, even when higher temperatures were used. We use toluene and ethanol (9:1) as solvent, because this combination remarkably reduced the palladium leaching [13,25].

It was found that PEG 15000 showed the best reactivity to the Heck reaction. When PEG 1000 was applied as the reaction medium, the yield was decreased (entry 18, Table 1), which could be attributed to the less stabilizing effect to nano-Pd and lower reducing reactivity of short chain length PEG to Pd(II) [13]. The optimized conditions were applied to Heck reactions between styrene and methyl acrylate with various aryl iodides and bromides (Table 2). As shown in Table 2, styrene was more reactive than methyl acrylate when using the same aryl halide.

The results obtained demonstrate moderate efficiency of Pd/PEG 15000 as a catalyst in the Heck reaction. In another study, Pd-PEG (prepared by loading $Pd(OAc)_2$ into the PEG matrix) [13] was tested in the Heck reactions of aryl halides with olefins and gave high yields of products, which is comparable with our results employing Pd/PEG 15000 in the same reactions.

The recovery and reusability of the catalyst were investigated using the reaction of iodobenzene with styrene as a model system. After the reaction was completed, the solvent was removed and the product was extracted into diethyl ether and separated by a simple decantation. The Pd/PEG 15000 catalyst is immiscible in ether and could be easily

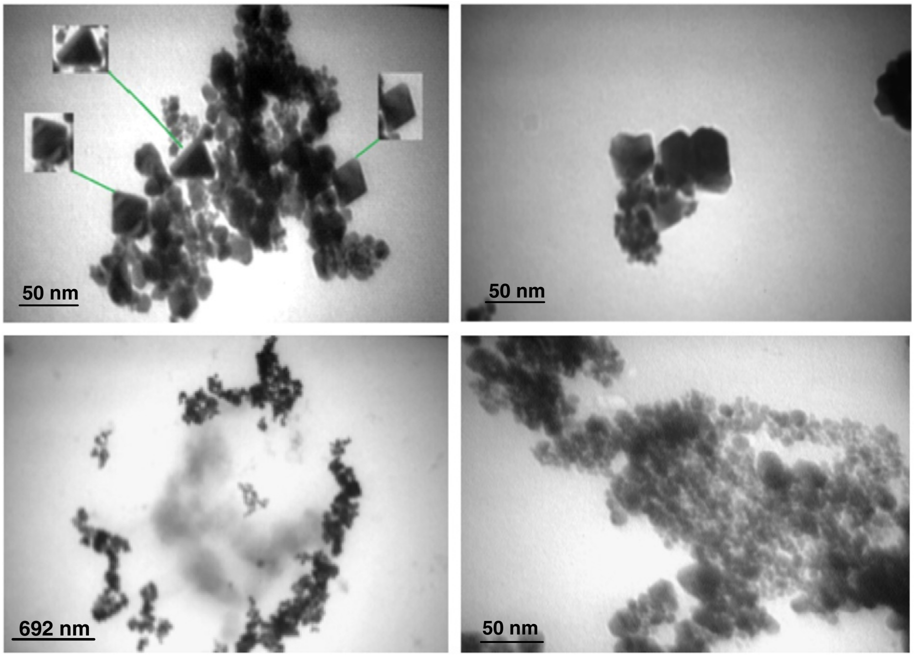


Fig. 2. a) (top) TEM micrographs showing typical shapes of Pd nanoparticles in the Pd/PEG 15000: triangular and rhombohedral (left), pentagonal and unidentified (right). b) (bottom) TEM images of Pd/PEG 15000 after its use as catalyst in the Heck coupling reaction.

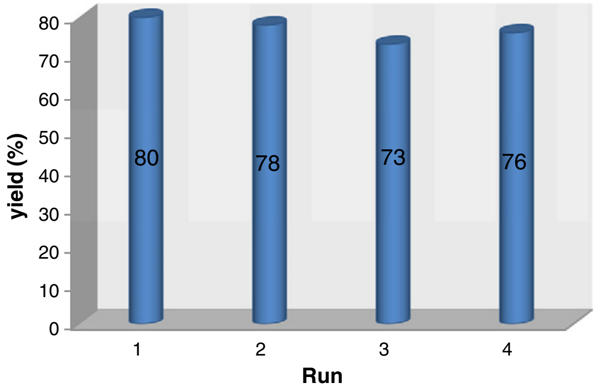


Fig. 3. A recyclability test for Pd/PEG 15000 in Heck cross-coupling reaction of iodobenzene with styrene (reaction conditions are the same as given in Table 2).

recovered and used for the next reaction cycle. The recycled catalyst was then used in the model reaction under the conditions mentioned in Table 2, giving 80, 78, 73 and 76% yields (Fig. 3).

The leaching of palladium in the recycling of the Pd/PEG was detected by ICP-OES analysis and the result was presented in Table 3. These data indicated that the extent of leaching of the palladium species was extremely low. This result demonstrates that the Pd/PEG 15000 catalyst may have practical utility.

Fig. 2(b) shows the TEM image of the PEG stabilized Pd(0) nanoparticles after their use as catalyst in the Heck coupling reactions. It was found that the size of the palladium (0) nanoparticles had increased to 20–30 nm after the reaction, most probably, due to the agglomeration of the particles during the catalysis.

4. Conclusion

We have successfully prepared PEG supported NC palladacycle catalyst with no other stabilizer and reducing agent. PEG appeared to act as both reducing agent and stabilizer. The nano-Pd preparation process is very simple and “green”. The results of UV show that the PEG molecular weight has significant effect on reducing reactivity of polymeric matrix. Both XRD and TEM reveal that nanosized palladium was not only fabricated by reducing of PEG, but was stabilized suitably by PEG. Also Pd/PEG 15000 was relatively an efficient catalyst system for the Heck reaction. Furthermore, the catalyst is stable to the reaction conditions, oxygen-insensitive, and can be reusable with negligible leaching of palladium.

Table 3
Evaluation of palladium leaching in the recycling experiments.

Recycle number	1	2	3	4
Concentration (μg/mL)	0.16	0.77	0.21	0.25
Pd leaching (%)	0.034	0.16	0.043	0.052

The coupling of iodobenzene with styrene was taken as the model reaction. The amount of nano-Pd was 4.5 mmol% relative to the amount of iodobenzene.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.08.027.

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